EFFECT OF MODIFYING HOST OIL ON COPROCESSING

Paul E. Hajdu, John W. Tierney, and Irving Wender
Department of Chemical & Petroleum Engineering
University of Pittsburgh, 1249 Benedum Hall
Pittsburgh, PA 15261

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INTRODUCTION
The world's supply of petroleum crudes is becoming heavier in nature so that the amount of vacuum bottoms has been steadily increasing. Coprocessing of coal with these resids (1000°F+) is an attractive way of obtaining useful distillates from these readily available cheap materials. Petroleum resids and coals differ in several ways; coal is more aromatic with a lower H/C ratio, contains more inorganic material than found in heavy resids, is richer in oxygen, and has smaller clusters of organic material. Heavy oils are more aliphatic and less aromatic, have very little oxygen, somewhat smaller amounts of nitrogen, significantly more sulfur, and contain relatively small amounts of vanadium, nickel and iron, some of which are trapped in porphyrin structures.

The objective of this work is to pretreat the host oil in ways that would improve its performance in coprocessing with coal. The following are examples of some ways in which heavy oil could be made into a better host oil: converting aromatic structures to hydroaromatics capable of donating hydrogen to coal, cracking the heavy oil to lower molecular weight material that would be a better solvent, and removing metals, sulfur, and nitrogen.

Other investigators have found that coprocessing performance can be improved by pretreating the host oil. Takeshita and Mochida[1] showed positive results by using a petroleum pitch that had been hydrotreated at high pressure over a Ni/Mo/Al₂O₃ catalyst. A similar approach was taken by Sato and coworkers[2] who obtained high coal conversion and high distillable oil yields after a tar sand bitumen they were using was hydrotreated with a Ni-Mo catalyst. Curtis and coworkers[3,4,5] have shown the importance of hydrogen donor compounds in host oil for achieving high coal conversion. Hydroaromatic compounds (hydrogen on a naphthenic carbon at the alpha or beta position from the aromatic ring) are one class of hydrogen donor compounds that are important in coal liquefaction.

EXPERIMENTAL
The work reported here used a Venezuelan oil obtained from the Corpus Christi refinery of Citgo. Its properties are listed in Table I as are those of another heavy oil for comparison; the latter is a vacuum resid from a wide mixture of crudes, obtained from AMOCO. Two coals, Illinois No.6 and Wyodak subbituminous, were coprocessed with host oils; both coals were Argonne premium coal samples. Properties of the coal samples have been previously published[6].

Four pretreatments of the resid were conducted in a well-stirred 300 ml stainless-steel autoclave batch reactor. Table II lists conditions and yields for the runs. One pretreatment, subsequently referred to as Pretreatment-A, involved cracking the resid at 440°C under H₂, 1000 psig (cold), for 2 hrs; molybdenum naphthenate (MN), supplied by ICN Biomedical Inc, and elemental sulfur, were added at a level of 1000 ppm Mo to suppress coke production to below 3 wt% (in runs made without MN at these conditions, coke production reached levels above 11%). The other three pretreatments involved hydrogenating the resid at milder conditions where cracking is suppressed. In Pretreatment-B the resid was reacted at 375°C under H₂, 1000 psig (cold), for 5 hrs using 1000 ppm of MN. In Pretreatment-C the resid was treated using a finely dispersed Mo/Fe₂O₃/SO₄ catalyst[7,8] (2 wt%) at the same conditions used in Pretreatment-B. In Pretreatment-D the resid was dissolved in toluene and hydrogenated using a homogeneous catalyst, dicobalt octacarbonyl (Co₂(CO)₈), at 130°C for 2 hrs under 2600 psig of 1:1 synthesis gas. Friedman and coworkers[9] found this system to be effective for selectively hydrogenating polynuclear aromatic compounds to their hydroaromatic derivatives; e.g., anthracene to 9,10-dihydroanthracene and pyrene to 4,5-dihydropyrene.

Pretreated products were removed from the 300 ml autoclave and separated into three fractions. The workup procedure ensured maximum recovery of products while minimizing losses of lighter material. Light oils (bp < 195°C) produced during pretreatments at 440°C were removed by distillation at atmospheric pressure. Pretreatments made at 375°C and below, generally produced no light oils. In these runs, distillation was not necessary. Products not removed by distillation were recovered by washing the contents of the reactor with THF. After filtration the THF was removed by distillation. Because the boiling point of THF is well below that of the pretreated heavy oils, good separation was possible. For runs made with Co₂(CO)₈, the THF-

washed products were refluxed for three hours to destroy the carbonyl. To further facilitate removal of the cobalt, silica-alumina powder was added to the liquid mixture prior to filtering. All THF-insoluble solids were vacuum dried overnight prior to weighing.

Coprocessing experiments were conducted in a horizontal, stainless-steel microreactor at 425°C for 30 min under 1000 psig (cold) H_2. Three weight ratios of host oil to coal were used; 9:1, 2:1 and 1:1. Most coprocessing runs were made with no added catalyst, but a few were made with either MN (2000 ppm Mo) or 2 wt% $Mo/Fe_2O_3/SO_4$, plus elemental sulfur. Products from the microreactor were recovered and separated into three fractions; pentane-soluble oils, asphaltenes and THF-insoluble solids. Pentane was removed from the filtered oil by rotovapor under atmospheric pressure to prevent losses of light products. Under these mild separation conditions a small amount of pentane remained with the oil. This was later measured by simulated distillation.

Gases were analyzed using an HP 5880A GC. Pentane-soluble oils (free of ash and asphaltenes) were analyzed using an HP 5890 series II GC/HP 5970 mass selective detector. A boiling curve for pentane-soluble oil samples was determined by simulated distillation[10] using an HP 5890 series II GC. Original and pretreated oil samples were analyzed by ^{1}H NMR spectroscopy using a Bruker 300 MSL spectrometer; samples were prepared in deuterated chloroform with tetramethylsilane for internal reference.

Catalytic dehydrogenation was used to measure the "available" hydrogen of resids and pretreated oils. Available hydrogen was defined as the amount of hydrogen gas evolved when an oil sample dissolved in phenanthridine was catalytically dehydrogenated for 285 min over a reduced $Pd/CaCO_3$ catalyst at atmospheric pressure.

Metal contents (Ni, Fe and V) of selected samples were determined by The Pittsburgh Applied Research Corp. using the ICP technique. Elemental analyses were conducted by Galbraith Laboratories Inc. and CONSOL Inc.

RESULTS AND DISCUSSION

Table III lists properties of the pretreated Citgo host oils. The Pretreatment-A oil was lighter, based on wt% of distillate, than the untreated resid as well as the other pretreated host oils. This is a result of the higher pretreatment temperature used. The available hydrogen content of the pretreated oils was higher than that of the untreated resid, which had a value of 9.8 H atoms/100 C atoms. This infers that the pretreated oils contain more donatable hydrogen. The increase in available hydrogen for the oils from Pretreatments B, C and D was slightly below the amount of hydrogen consumed during these runs, indicating significant hydrogen utilization. All pretreated host oils, with exception of the Pretreatment-D oil, had higher H/C atomic ratios than that of the untreated resid; although the increases were not large. The pretreated host oils had lower sulfur concentrations than the untreated resid; nitrogen concentrations remained unchanged.

Figure 1 shows the effect of coal slurry concentration on Illinois No.6 coal conversion to THF-solubles in thermal (no added catalyst) coprocessing runs made with the different host oils. Coal conversion was calculated from the amount of unconverted (THF-insoluble) material recovered from the products after correcting for ash, added catalyst and petroleum-derived coke (this was less than 3 wt% based on repeat runs made without coal). The Figure shows that coal conversions in the oils from Pretreatments B-D were higher than levels achieved in the untreated Citgo resid or the oil from Pretreatment-A. Coal conversions in the Citgo resid and in the oil from Pretreatment-A decreased as the concentration of coal in the feed was increased. This trend has been observed by other investigators[11,12] demonstrating the limited ability of these host oils to bring about coal dissolution. On the other hand, coal conversions in the oils from Pretreatments B-D appeared to be independent of coal slurry concentration up to 50 wt%. Illinois No.6 coal conversion in these pretreated host oils were slightly higher than conversions obtained when the coal was catalytically coprocessed in the Citgo resid using either MN (2000 ppm) or $Mo/Fe_2O_3/SO_4$ (2 wt%). These results clearly demonstrate that the host oils from Pretreatments B, C and D are good coprocessing solvents. When these host oils were coprocessed with coal in the absence of hydrogen gas, conversions were significantly less than levels achieved under hydrogen gas.

Figures 2 and 3 show how distillable product yields varied with coal slurry concentrations when Illinois No.6 coal was coprocessed with the untreated resid and the oil from Pretreatment-C, respectively. Distillable product yields are defined as the wt% of ash-free feed converted to gases and pentane-soluble oil that had a simulated distillation boiling point below 565°C. The lower line in the Figures represents the contribution from the host oil assuming no interaction

between coal and host oil. This line was drawn by assuming the distillate yield from the host oil obtained at zero coal concentration did not change. The shaded area above the lower line represents the contribution of distillable product from coal. This value was based on the yield from a thermal coal liquefaction run made with Illinois No.6 and the solvent diphenylmethane. During the run, 84.5% of Illinois No.6 coal was converted to THF-soluble products, of which an estimated 50% was distillable. Rahimi and coworkers[12] also concluded that up to 40-50 wt% of converted coal ends up in the distillate (bp < 525°C).

At coal slurry concentrations below 50 wt%, distillable product yields were generally above the level calculated assuming no interaction between coal and host oil, with exception of runs made with the oil from Pretreatment-A (not shown), which yielded distillate below this level. These results show a possible synergism between coal and host oil, a behavior that has been reported[11,12,13] by others.

CONCLUSIONS

We have found that mild pretreatment of a Citgo resid (1000°F) using either Mo naphthenate or $Mo/Fe_2O_3/SO_4$, as well as a pretreatment using the homogenous catalyst $Co_2(CO)_8$ under synthesis gas can increase the available (donatable) hydrogen content of the resid. When these pretreated oils were thermally (no added catalyst) coprocessed with an Illinois No.6 coal, about 90 wt% of the coal (maf) was converted to soluble products. This high coal conversion was realized even at a high coal loading of 50 wt%. Pretreatments at 440°C, that crack the resid without adding much available hydrogen, showed little promise for improving coal conversion above levels achieved with untreated resid. The products from coprocessing coal and oil were equally split between high boiling material, mostly asphaltenes, and distillate. Distillate yields appeared to be affected by the concentration of coal in the feed, with maximum yields at coal loadings below 50 wt%.

ACKNOWLEDGEMENTS

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Table I. Properties of Petroleum Resids (1000°F+)

	Citgo Resid	Amoco Resid
C, wt%	85.4	84.3
H, wt%	10.1	10.2
S, wt%	3.4	4.6
N, wt%	0.8	0.5
O, wt%	0.3	0.4
Atomic H/C	1.42	1.45
V, ppm	555	251
Ni, ppm	110	57
Fe, ppm	12	13
Pentane Insolubles, wt%	27.3	20.1
Aromatic Carbons[a], fraction	0.33	0.32

a: Based on ^{1}H NMR by Brown and Ladner's method[14]

Table II. Reaction Conditions and Product Yields for Pretreatments of Citgo Resid

	Oil-A	Oil-B	Oil-C	Oil-D
Catalyst, concentration	MN, 1000 ppm	MN, 1000 ppm	Mo/Fe$_2$O$_3$/ SO$_4$,2 wt%	Co$_2$(CO)$_8$, 6.2 wt%
Atmosphere	H$_2$	H$_2$	H$_2$	CO/H$_2$ (1:1)
Temperature, °C	440	375	375	135
Pressure (cold), psig	1,000	1,000	1,000	2,000
Time, hrs	2	5	5	2
Gas yield, wt%	10-25	1-12	3	0
Oil yield, wt%	72-87	86-97	95	100
Coke yield, wt%	3	2	2	0

Table III. Properties of Citgo Pretreated Host Oils

	Oil-A	Oil-B	Oil-C	Oil-D
b.p. < 565°C[a], wt% b.p. > 565°C, wt%	62.6 37.4	29.7 70.3	33.3 66.7	17.9 82.1
C, wt%	85.1	85.9	85.6	83.7
H, wt%	10.6	10.4	10.8	9.7
S, wt%	2.2	2.7	2.9	2.8
N, wt%	0.9	0.9	0.8	0.8
O, wt%	1.2	0.1	0.0	3.0
Atomic H/C	1.49	1.45	1.51	1.39
V, ppm	392	----	477	----
Available[b] Hydrogen per 100 C atoms	12.4	16.8	14.0	17.5

a: b.p. < 565°C consists of pentane-soluble oil having a simulated distillation b.p. < 565°C (1050°F). b.p. > 565°C consists of pentane-insoluble asphaltenes, and pentane-soluble oil having simulated distillation b.p. > 565°C.
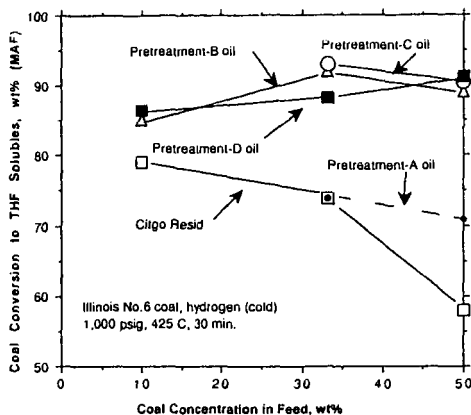b: Value based on catalytic dehydrogenation, experiment described in text.

Figure 1. Effect of coal concentration on Illinois No.6 coal conversion to THF solubles in thermal coprocessing with Citgo resid and pretreated host oils (Pretreatment-A: 1000 ppm MN, 440°C, 1000 psig (cold) H_2, 2 hr reaction time; Pretreatment-B: 1000 ppm MN, 375°C, 1000 psig (cold) H_2, 5 hr reaction time; Pretreatment-C: 2% Mo/Fe$_2$O$_3$/SO$_4$, 375°C, 1000 psig (cold) H_2, 5 hr reaction time; Pretreatment-D: 6.2% Co$_2$(CO)$_8$, 135°C, 2650 psig CO/H_2 (1:1), 2 hr reaction time).
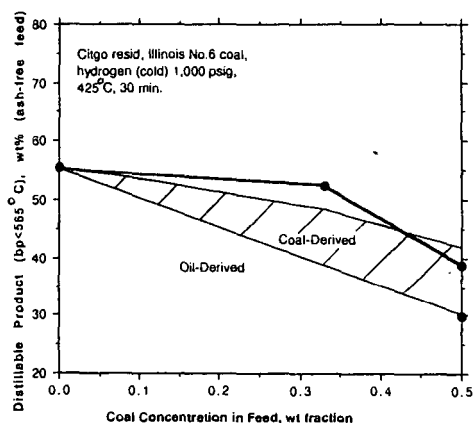

Figure 2. Effect of coal concentration on distillable product yields in coprocessing Illinois No.6 coal with Citgo resid.
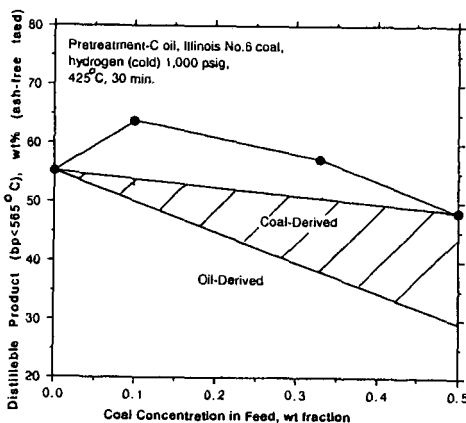

Figure 3. Effect of coal concentration on distillable product yields in coprocessing Illinois No.6 coal with pretreatment-C (2% Mo/Fe$_2$O$_3$/SO$_4$, 375°C, 1000 psig (cold) H_2, 5 hr reaction time) oil.

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